The Source, Cycling, and Behavior of Chromophoric Dissolved Organic Matter in Coastal Waters

Mark L. Wells
School of Marine Sciences
University of Maine
Orono, ME 04469-5741
phone: (207) 581-4322 fax: (207) 581-4388 email: mlwells@maine.edu

Jennifer Boehme
School of Marine Sciences
University of Maine
Walpole, ME 04573
phone: (207) 563-3146 fax: (207) 581-4388 email: jboehme@maine.edu

Grant Number: N00014-05-1-0116
http://www.marine.maine.edu/~wellsm/Homepage.htm

LONG-TERM GOALS

Our long term research goal is to ascertain the nature and magnitude of optical effects (absorbance / fluorescence / scattering) in surface seawaters associated with the production and cycling of marine colloidal organic matter. We are particularly interested in determining how these effects are driven or modulated by the productivity dynamics of phytoplankton and marine heterotrophic bacteria in coastal regions not directly influenced by high riverine inputs of terrestrially-derived materials.

OBJECTIVES

Marine chromophoric dissolved organic matter (CDOM) imparts highly variable optical signatures in surface waters over short spatial and temporal scales for reasons not yet understood. While considerable research efforts currently are underway on the absorption and fluorescence characteristics of bulk CDOM and FDOM (< 0.2-0.7 µm), our primary objective is to follow the chromophoric signatures of different molecular weight fractions to ascertain how production (or allochthonous input) and removal of colloidal organic matter contributes to the high variability in bulk CDOM. A signficant fraction (10-40%) of dissolved organic matter is colloidal in size (1-1000 nm), and this fraction is reactive to photodegradation and bio-degradation (to soluble substances) as well as aggregation (to large sinking particles). Marine colloids are inhomogeneous in their optical characteristics, and the abundance of colloidal matter can change rapidly in association with in-situ biological processes. Our objective is to determine to what extent the dynamic, opposing processes of production and degradation of colloidal CDOM influences the behavior of CDOM and FDOM in surface seawaters, and with that knowledge develop forecasting insights to the optical characteristics of nearshore waters.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2006	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
The Source, Cycling, and Behavior of Chromophoric Dissolved Organic Matter in Coastal Waters	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **School of Marine Sciences University of Maine Orono, ME 04469-5741**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**10**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

APPROACH

Our work over the last year have focused mainly on field studies aimed towards understanding how the optical characteristics of soluble and colloidal organic matter change under different phytoplankton growth conditions and vary among estuaries, coastal shelf regions and in offshore waters where phytoplankton blooms are stimulated. The sites we have used are the marine regions of the Damariscotta River estuary (Maine), the inner and outer continental shelf regions off the Juan de Fuca Strait and central British Columbia, and in the eastern subarctic Pacific. The latter two study regions were sampled during cruises of opportunity.

We employ two analyical approaches to study marine CDOM; a size fractionation technique and a statistical approach to categorizing the fluorescence characteristics of the bulk CDOM. We use Flow Field-Flow Fractionation (Flow FFF) to partition CDOM into a continuum of molecular weight sizes. Briefly, a flow field is applied at right angles to the channel flow within a shallow (~200 μm) ribbon-like chamber. Soluble fractions are driven through the membrane (1 KDa) on the accumulation wall, while colloidal components are driven to the accumulation wall. The resultant concentration gradient is opposed by diffusion (a function of colloidal size), resulting in colloids of different size being retained in different stream laminae. Unequal laminae velocities due to shear along the accumulation wall causes a well-defined separation of different colloidal size fractions according to the mean colloid proximity to the wall, which then is measured by UV absorption after the sample stream exits the flow chamber. Limitations of detection sensitivity has required that the entire colloid fraction be concentrated before analysis. We use on-line focusing, whereby seawater (1-50 ml) is "focused" at the head of the channel before proceeding with the normal analysis mode. A single wavelength detector (254 nm) has been primarily used for quantifying CDOM. Atlhough this wavelength is lower than normally used for CDOM measurements, it provides the higher sensitivity needed to detect the colloidal sub-fractions in these highly diluted samples.

We measure the absorbance characteristics of collodial CDOM by interfacing the channel outflow of FlowFFF to a 50 cm waveguide/CARY 50 spectrophotometer system. In this way we are able to obtain multiple absorbance scans across the CDOM size continuum. The resultant slope data are contrasted to the absorbance spectrum of the bulk dissolved sample. Subsequently, outflow from the waveguide is collected in batch for analysis by excitation emission matrix spectroscopy (EEMS), with countour surface plots providing 3D fingerprints of fluorescent dissolved organic matter (FDOM) collected for different sample aliquots. EEMS has been shown to be an effective means for distinguishing between types of organic matter in seawater. In addition, absorbance scans are measured on each sample aliquot across the same excitation range to both characterize the absorbance characteristics and to enable the relative fluorescence efficiencies to be estimated. As a consequence, we are able to analyze the absorbance and fluorescence characteristics of different colloidal size fractions during a single sample run, and compare them with the charateristics of the bulk dissolved (<0.4 μm) CDOM. The two objectives are to determine the extent that marine colloid cycling influences the optical signature of surface seawaters, and to compare EEMs signatures of different seawaters in relation to the colloidal contributions.

The key individual assisting us with this work is Sheri Floge (Research Specialist) who is responsible for overall laboratory activities, Flow-FFF operation, and measurements of the CDOM absorbance.

WORK COMPLETED

We continue to make advances on several aspects of our research objectives. Our primary field sampling site continues to be the marine waters of the Damariscotta River estuary, where we completed a long term sampling program to measure the seasonal variations in colloidal CDOM associated with measured changes in phytoplankton abundance. These measurements include size distribution of colloidal matter, the differences in spectral absorbance (~300-600 nm) and fluorescence signature (excitation emission matrix spectroscopy) with colloidal size. The purpose here is to establish a dataset on how the combined effects of non-point source terrestrial runoff and phytoplankton production influences the bulk and size distribution of CDOM and FDOM. We contrast this weakly estuarine, productive system with upwelling and non-upwelling shelf waters (Juan de Fuca eddy and associated waters off Vancouver Island and central British Columbia), and offshore waters of the iron-limited eastern subarctic Pacific using cruises of opportunity. This year we participated in one major cruise to these latter regions. The purpose is to determine how colloidal CDOM characteristics and cycling change with phytoplankton blooms across diverse regions to ascertain whether general patterns exist. The coastal regions off Vancouver Island and central British Columbia provide an excellent contrast to the confined, phytoplankton and macroalgal influenced Damariscotta estuary because it contains discrete surface waters influenced by upwelling, high in-situ primary production, general continential and offshore inputs. The central British Columbia coast also is a region that creates mesoscale eddies which combine offshore and shelf waters before spinning off into the eastern subarctic Pacific. This year, EEMS analyses again were performed on-board the vessel on freshly collected samples. In addition to studying spatial variations, vertical profiles also were analyzed, providing an opportunity to examine the differences in the character of CDOM and FDOM upwelling with deep waters compared to that generated by phytoplankton production. Analysis of these data have not yet been completed, however, these results will provide valuable end-member characteristics for elucidating how much of the CDOM characteristics in nearshore coastal waters should be attributed to marine vs. terrestrial origins.

These field programs have enabled us to continue expanding our database of EEMS from different coastal and oceanographic regions. We are statistically assessing the similarities and differences among colloidal size fraction and bulk CDOM using Principle Component Analysis. Variability within the data set is decomposed into a series of linear terms that can be used to evaluate the relative importance of changes in fluorescence bandwidth and wavelength shifting across size fractions and due to various processes such as dilution and bacterial or photochemical alteration. The intention here is to use these statistical groupings of optical characteristics according to water types (e.g., surface, mid-depth, deep, inshore, offshore) and locations (e.g., Gulf of Mexico, coastal Maine, Washington State waters, etc.) to develop a forecasting tool for predicting optical characteristics of a given nearshore region from knowledge of the physical mixing processes and the predominant source waters.

In this final year of the project we have developed a synthesis of the colloidal and bulk seawater experiments and field measurements. This synthesis provides an assessment of the production and loss of colloidal CDOM with respect to phytoplankton production and seasonal non-point source terrestrial runoff as well as the effects of biological and photochemical degradation on the optical characteristics of colloidal and bulk CDOM.

RESULTS

Although the project comprises a large number of experiments and field programs, we focus on three central hypotheses in this report. Our finding highlights and a summary of implications are presented.

Hypothesis 1 —The size distributions of colloidal CDOM vary seasonally in conjunction with pre- and post-bloom stages and these patterns contrast with times when terrestrial runoff is significant.

1. The smallest of the colloidal CDOM fractions (~1-18 kDa in size) is highly labile with very short residence times in the dark (hours), most often has a protein-like fluorescence character, but nevertheless is maintained at elevated concentrations during high phytoplankton conditions. It appears then that this persistent CDOM fraction is maintained by a dynamic balance between production and degradation/loss.

2. The major source of this small colloidal fraction is marine phytoplankton during spring, summer and fall. There is little terrestrial source during the bulk of the year (i.e., no relationship between small colloidal CDOM and salinity, but a reasonably good one with chlorophyll).

3. The small colloidal CDOM also is highly susceptible to photochemical degradation while larger colloids phases are comparatviely resistant.

4. In early winter, there is a sharp increase in small colloid CDOM abundance associated with runoff, but the residence time of this material is very short, indicating that the rapid removal of this matter was not replenished by in-situ processes (in contrast to periods of active phytoplankton production).

5. The small colloidal CDOM associated with terrestrial inputs had similar optical characteristics (based on EEMS and spectral slope) to that associated with phytoplankton production. However, the bulk (unfiltered) CDOM characterisitcs changed significantly. In other words, the terrestrial effects on marine CDOM in this region appears to be predominantly due to changes in the truly soluble CDOM components, and is not reflected across the broad spectrum of CDOM sizes.

6. This runoff-associated increase in colloidal CDOM was not observed in early spring, indicating that seasonally dependent terrestrial processes must be taken into account when modeling the contributions of small colloidal CDOM to the optical characterisitcs of seawater.

7. The large colloidal CDOM fraction (~18-350 kDa) is much less labile (i.e., is relatively stable in the dark) and it has a more humic-like optical signature (EEMS and spectral slope). The persistence of this larger colloidal CDOM in coastal waters then is indicative of a low rate of supply.

8. The abundance of the large colloid CDOM fraction also followed the seasonal distribution of chlorophyll concentrations, indicating that in these coastal waters in-situ processes also were the primary source of this CDOM. However, in increases in abundance associated with periods of high runoff in early winter were muted with respect to the small colloidal CDOM fraction. Overall, this fraction is more stable chemically and it has less dramatic fluctuations in abundance and optical characteristics over the seasonal cycle.

Interpretation: A sub-fraction of CDOM having unique optical characteristics has the potential to change rapidly, particularly early in the season before the spring bloom, and in the fall after phytoplankton production (i.e., chlorophyll concentrations) begin to drop. Abundances during late spring (after the spring bloom) and summer are relatively closely tied to total chlorophyll concentrations. However, the abundance of colloidal CDOM can fluctuate wildly in winter, with increases being associated with increased runoff but rapid (days) return to low levels when runoff drops. The larger colloidal CDOM fraction was better correlated to chlorophyll concentrations indicating that predicting the contribution of this fraction to CDOM signatures in coastal surface waters might be acheivable by remote sensing.

Hypothesis 2 — Photochemical degradation of CDOM in soluble and colloidal size fractions proceeds non-uniformly, with soluble and small colloidal chromphores being the most susceptible to photolysis.

1. This hypothesis has been verified in replicate experiments showing that the small colloidal CDOM fraction is more susceptible to photodegradation, as measured by changes in CDOM absorption and increases in S, than larger colloidal CDOM size fractions.

2. Photodegradation of colloidal CDOM is not spectrally uniform, as measured with EEMS. Loss of protein-like fluorescence fractions is more prevalent than loss of the humic portions of the spectra.

3. Paradoxically, while the larger colloidal CDOM fractions show photodegradation under full sunlight, the remaining colloidal CDOM has a *lower* spectral slope (i.e., opposite that seen in bulk CDOM and in the small colloidal CDOM fraction). These changes may reflect enhanced absorption of low molecular weight substances, or the photochemically-enhanced photochemical fragmentation of colloidal CDOM larger than quantified with our FlFFF method.

Interpretation: Photochemical processing of colloidal CDOM proceeds differently than truly soluble colloidal fractions. Predicting these impacts on the optical signature of surface seawaters should depend on the seasonally-dependent abundance of colloidal CDOM associated with in-situ phytoplankton blooms.

Hypothesis 3 — The fluorescent and absorption signatures of near surface coastal waters can be predicted based on knowledge of the source water masses and their optical characterisitics.

1. Our limited sampling to date shows that CDOM fluorescence data (EEMS) can provide a statistically significant fingerprint of different water masses within the same geographical region. The key to accomplishing this level of discrimination is the use of Principal Component Analysis on a large enough database to achieve statistical significance.

2. The temperature and salinity profiles in coastal upwelling waters off the Strait of Juan de Fuca and Washington State showed the presence of three distinct water masses in the near surface region (<50 m). PCA analyses identifed unique optical characteristics within EEMS measured in these water masses that are consistent with the broader database for surface, mid-depth and deep ocean waters.

Interpretation: If different water masses indeed have statistically identifiable optical features, and the bulk of these features are comparatively stable, then the optical characteristics of a given coastal water column can be predicted with knowledge of the physical oceanographic conditions (mixing of water

masses) and the optical characteristics of the source waters. These, in turn, will be modulated in the photic zone by phytoplankton processes as described above.

IMPACT/APPLICATIONS

These findings address two unknowns surrounding marine CDOM; identifying the biogeochemical factors regulating the composition and spectral characteristics of CDOM, and the goal of predicting the optical characteristics of coastal waters over short (1 week) time intervals. We have made significant progress in both of these areas. Better definition of the coupling between CDOM and colloidal processes and, in turn, the linkages between colloidal composition and the contributions of phytoplankton-associated production and small terrestrial inputs (relative to large river systems), provides key insight to the factors influencing CDOM abundance and character. Combining the use of excitation emission matrix spectroscopy with statistical database analysis tools (Principal Component Analysis) provides evidence that the optical characteristics of near surface waters may be predicted from knowledge of the source waters, their respective optical signals, and the general oceanography of a given coastal region. Though preliminary, these data to our knowledge provide some of the best insights on how to gain the predictive capability sought by scientists to assist in the remote characterization of spectral components of surface coastal waters.

The picture that emerges from our work is that a significant fraction of the CDOM and FDOM component in different seawaters are associated with the marine colloidal phase, and this fraction is a dynamic pool that can change over time scales ranging from days to months. These changes are associated with phytoplankton production and unidentified processes linked to freshwater influences in coastal waters. Colloidal CDOM optical characteristics, including both spectral absorption and fluorescence via excitation emission matrix spectroscopy (EEMs), vary as a function of size, likely due to rapid cycling by microbial processes. In addition to biological processes, exposure to sunlight leads to non-uniform degradation across the size spectrum of colloidal CDOM. Exposure-dependent effects reversed the expected trends of the spectral slope of the remaining CDOM. These results provide a rich backdrop of data from which to develop predictive insights on marine CDOM input, removal and cycling in nearshore waters removed from overwhelming inputs of terrestrially-derived CDOM.

RELATED PROJECTS

None

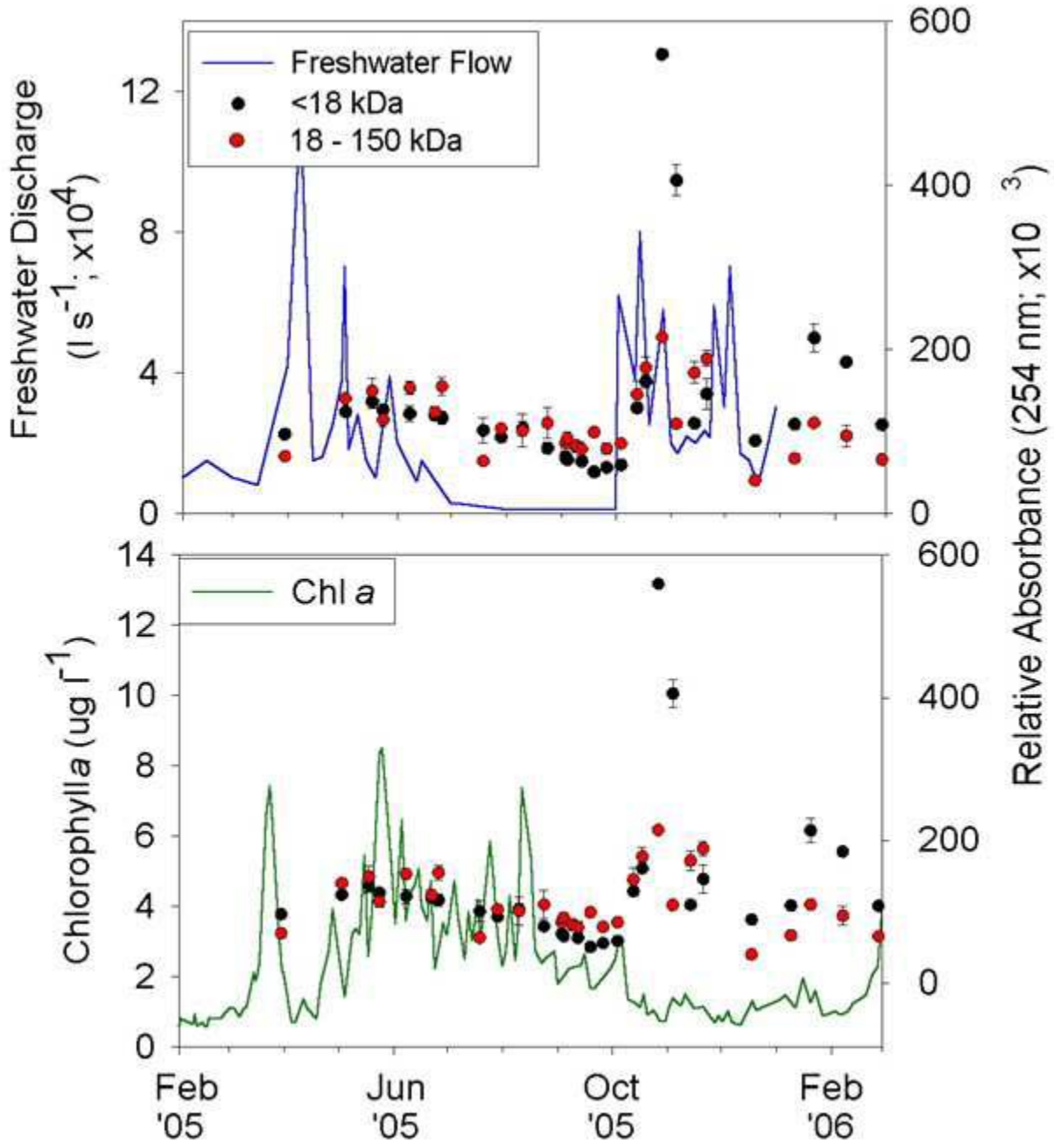

Figure 1. The relationships between small (<18 kDa) colloidal CDOM (black circles), large (18-150 kDa) colloidal CDOM (red circles) and freshwater discharge from the Sheepscott River, adjacent to the Damariscotta River estuary (Top Panel) and surface chlorophyll concentrations (Bottom Panel). [The relative abundances of small and large colloidal CDOM are similar during the spring, summer and early fall, tracing the temporal pattern in chlorophyll concentrations (bottom panel), but not freshwater discharge (top panel). In late October, river discharge increased sharply, coincidence with a decrease in chlorophyll concentrations. Colloidal CDOM concentrations jumped significantly in conjunction with the fall runoff, and became much less stable compared to earlier in the season.]

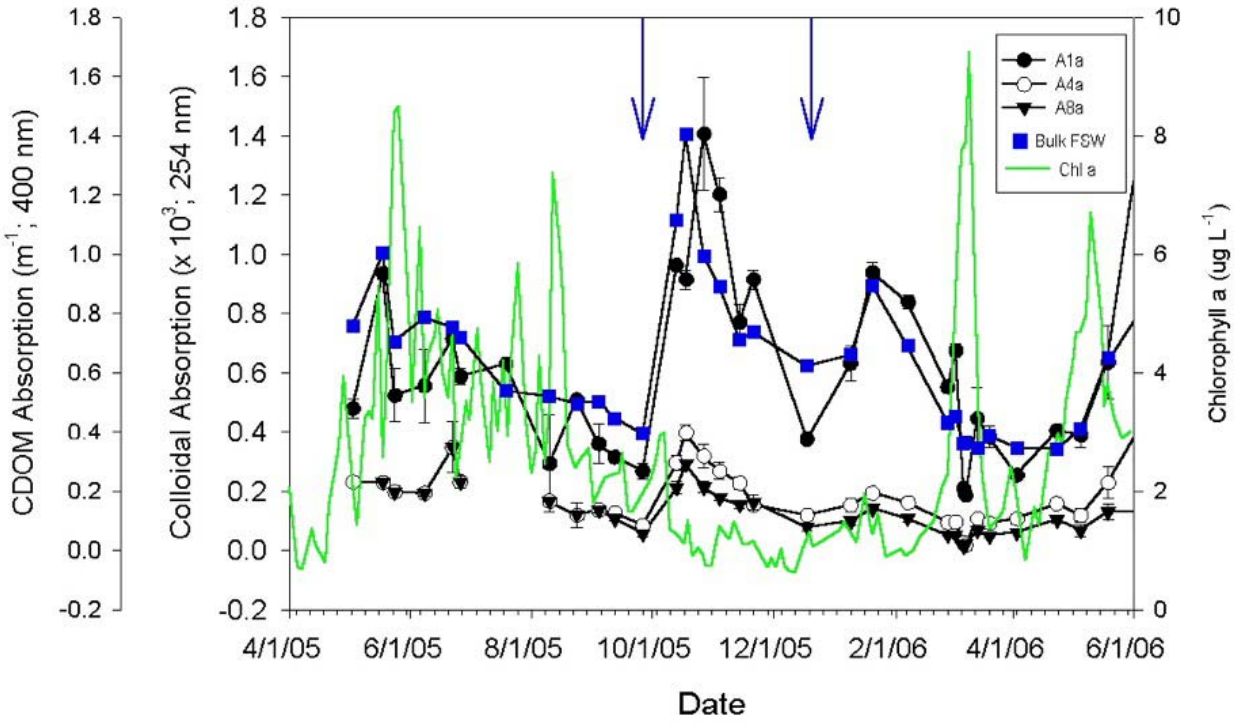

Figure 2. Changes in CDOM measured in bulk seawater (at 400 nm) and three colloid size fractions (A1 - < 5 kDa; A2 – 5-10 kDa; A3 – 10-15 kDa) in relationship with chlorophyll concentrations (green line) and total dissolved CDOM (blue squares). Marked high precipitation events are depicted by the vertical arrows. [The annual cycle of bulk (unfiltered) and colloidal CDOM tend to follow that of chlorophyll concentrations in spring and summer, but increase sharply during winter months. The smallest colloidal phase (<5 kDa) followed closely the abundance of bulk CDOM, while larger colloidal CDOM had lower overall concentrations and displayed different temporal patterns in abundance.]

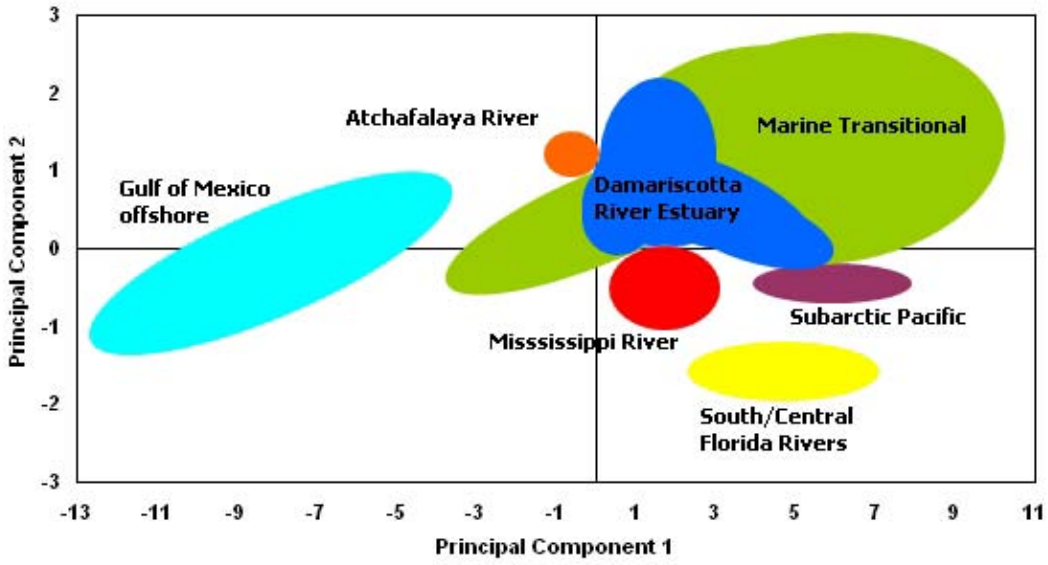

Figure 3. Principal Component Analysis plot showing the breakout distribution of EEMs data according to their statistical associations or differences. [Statistical grouping of waters having similar fluorescence characteristics show marked degrees of unique signatures as indicated by non-overlap of statistical blots. In theory, these plots can be used similar to oceanographic T/S plots to determine relative mixing ratios of regional members based on their optical characteristics.]

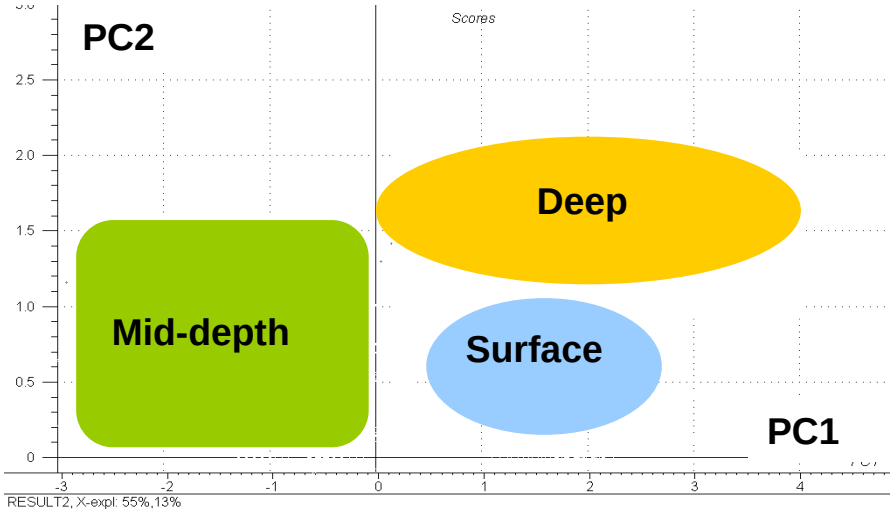

Figure 4. Component Analysis score plot for a subset of samples collected from the Juan de Fuca eddy region off the Washington coast. [The regions identified above display the separation in statistical space for EEMs obtained from surface, mid-depth and deep ocean waters in this general coastal region. The clear separation suggests that it may be possible to predict the optical characteristics of coastal waters based on the relative mixtures of their source waters.]

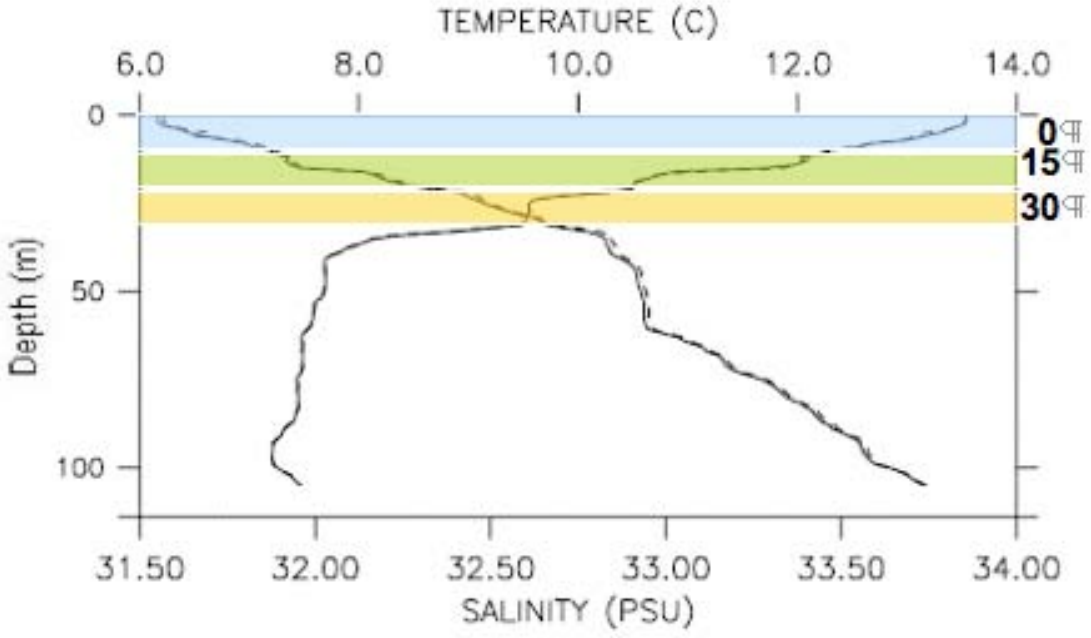

Figure 5. Depth profiles of temperature and salinity in nearshore Juan de Fuca waters overlaid with the EEMs-derived indications of the source waters. [Profiles of temperature and salinity show the presence of three broadly distinct water types in the upper 30 m of this upwelling region. PCA statistical groupings of surface, mid-depth and deep waters obtained from numerous samples in this region suggest that these water types can be correctly assigned by their optical characteristics.]